

Some Double Halides of Cadmium with
the Methyamines and Tetra-
methyllummonium

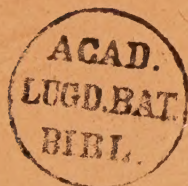
DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

CHARLES DABNEY RAGLAND

1897



EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.
1897.

Some Double Halides of Cadmium with
the Methylamines and Tetra-
methyllummonium

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

CHARLES DABNEY RAGLAND

1897



EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.
1897.



Digitized by the Internet Archive
in 2026

CONTENTS.

Acknowledgment	4
Introduction	5
Preparation of Material	8
Methods of Analysis	9
Preparation of the Double Salts	10
Compounds Described.....	10
Methylamine Salts.....	11
Double Chlorides	11
Double Bromides	12
Double Iodides.....	13
Dimethylamine Salts.....	13
Double Chlorides	13
Double Bromides.....	16
Double Iodides.....	18
Trimethylamine Salts.....	18
Double Chlorides	18
Double Bromides.....	20
Double Iodides.....	21
Tetramethylammonium Salts.....	22
Double Chlorides	22
Double Bromides.....	23
Double Iodides.....	24
Conclusions.....	25
Biographical	26

ACKNOWLEDGMENT.

This investigation was undertaken at the suggestion of Professor Remsen, and I would here express to him my sincere thanks for his constant supervision and wise counsel at every stage of the work.

I would also thank Prof. Morse and Dr. Mathews for their instruction and advice so freely given in lecture room and laboratory.

SOME DOUBLE HALIDES OF CADMIUM WITH THE METHYLAMINES AND TETRA- METHYLAMMONIUM.

INTRODUCTION.

For a number of years investigations have been carried on in this laboratory with a view to throwing more light on the vexed question of double halides.

That compounds of this class exist, and are well characterized chemical individuals, has been recognized by chemists from the early history of the science.

Most investigators have been content to dismiss them as "molecular compounds." This term has come down to us from a period when it was thought necessary to make a sharp distinction between atomic or true chemical compounds, which the valence hypothesis was competent to explain, and molecular compounds whose structure was more obscure.

Speculations as to the probable structure of the so-called "molecular compounds" have not been wanting. From time to time striking analogies have been drawn between them and compounds better understood.

In 1826, Von Bonsdorff¹ suggested that just as basic and acidic oxides unite to form salts, in all probability basic and acidic halides may form analogous salts, which differ from the first class mentioned in containing a halogen in place of oxygen.

Boullay,² in the same year, advanced, independently, the idea that just as oxides unite to form oxygen salts and sulphides to form sulpho-salts, so halides combine and form more complex salts.

Liebig³ and Berzelius⁴ both opposed this idea on the ground that salts cannot have both basic and acidic properties.

¹ Ann. chim. phys., **34**, 142 (1826).

² Ann. chim. phys., **34**, 337 (1826).

³ Ann. chim. phys., **35**, 68 (1827).

⁴ Berz. Jb., **8**, 138.

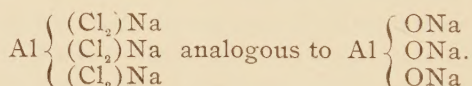
The influence of these two eminent chemists prevented the general acceptance of the views offered by Von Bonsdorff and Boullay, and until quite recently the striking analogies between double halides and oxygen salts seem to have been lost sight of.

Professor Remsen,¹ in an extended article on the "Nature and Structure of the Double Halides," has reviewed the whole field in a very thorough manner.

As a result of his investigations, he has shown that, with a few exceptions, the 400 or more double halides described in the literature can be grouped under a few simple types.

The following generalization, which is usually designated in the literature as Remsen's Law, was the result of these observations: "When a halide of any element combines with a halide of any alkali metal to form a double salt, the number of molecules of alkali salt which is added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms combined in the latter."

An explanation of this regularity, Professor Remsen thinks, can be found in the assumption that two halogen atoms together can play the same part that the so-called linking oxygen atom plays in the oxygen salts. According to this conception, then the structure of the double halide usually represented $\text{AlCl}_3, 3\text{NaCl}$ would be expressed



This view had been previously advanced by Naquet,² Blomstrand,³ Jörgensen,⁴ Mallet,⁵ Francke,⁶ and Hayes,⁷ but it did not meet with general acceptance.

The objections to this conception came from chemists who thought that the halogens had a constant valence, but in the light of the evidence we now have, which points unmistakably

¹ Am. Chem. J., **11**, 291.

² In his "Principes de chimie fondée sur les theories modernes."

³ In his "Chemie de Jetztzeit."

⁴ J. prakt. Chem., **16**, 352.

⁵ Am. Chem. J., **3**, 189 (1881).

⁶ J. prakt. Chem., **36**, 451.

⁷ Phil. Mag., **25**, 221, 297.

bly to the variable valence of these elements, there remains little ground for objection on this score.

Some of the double halides recorded in the literature not obeying the above law have a doubtful existence. In fact the interest awakened in this field by the paper of Professor Remsen has led to a careful consideration of a number of such doubtful cases with the result that no evidence could be found of their existence.

However, there are some well-known exceptions to the law as above stated, and subsequent work has shown that the formulæ have been correctly represented. Among these may be mentioned two examples: $\text{CdCl}_2 \cdot 4\text{NH}_4\text{Cl}$ and $\text{CuCl}_2 \cdot 2\text{KCl}$.

An extension of the law has been made¹ which covers such double halides. Three halogen atoms may be regarded as

playing the part of a trivalent group, thus: $-\text{Cl} \begin{array}{c} \diagup \text{Cl}- \\ | \\ \diagdown \text{Cl}- \end{array}$ and

$\text{CuCl}_2 \cdot 2\text{KCl}$ may be represented $\text{Cu}-\text{Cl} \begin{array}{c} \diagup \text{ClK} \\ | \\ \diagdown \text{ClK} \end{array}$.

In Professor Remsen's article, previously referred to, he is inclined to the view that considering the double halides of ammonium with metallic halides described in the literature, they seem to obey some law of their own. This conclusion was arrived at from a consideration of a number of double halides of ammonium and lead described by Andre.² This work has been repeated by Randall,³ Wells and Johnston,⁴ and others. No evidence was found for the existence of double salts which are not conformable to Remsen's law.

Fonzez-Diacon⁵ quite recently has taken up the investigation of the same subject, with special reference to mixed halides. In no case has he obtained salts which prove exceptions to the law.

It was thought, inasmuch as both cadmium and ammonium double salts have been the subject of special inquiry in refer-

¹ Am. Chem. J., **14**, 87.

² Compt. rend., **96**, (1883) 435; Bull. Soc. Chim. (Paris), **40**, (1883) 14; Ann. Chim. Phys. [6], **3**, 104.

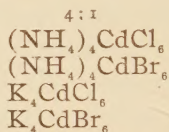
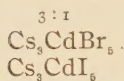
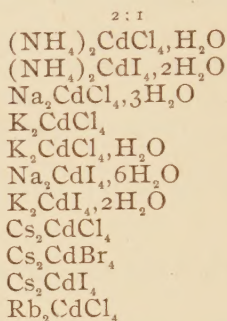
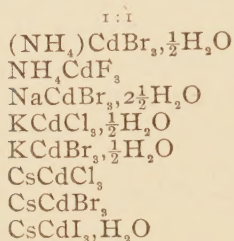
³ Am. Chem. J., **15**, 494.

⁴ Am. J. Sci. [3], **46**, 25.

⁵ Bull. Soc. Chim. (Paris), **17**, (1897).

ence to their relations to the above law, the double halides of cadmium with the substituted ammonium salts promised more than usual interest.

On beginning this investigation, the literature was carefully reviewed, and it is thought that most of the double halides of cadmium on record are comprised in the list which was made at that time. Of the 80 or more double salts included in this list, only those will be mentioned which contain the halides of the alkali metals and ammonium.



Preparation of Material.

Cadmium chloride and cadmium iodide were prepared by dissolving the metal previously tested for purity in the respective acids and evaporating the solutions to dryness.

Inasmuch as cadmium dissolves quite slowly in hydriodic acid, in a subsequent preparation of the iodide, cadmium oxide was used. This was prepared by igniting the oxalate, which was precipitated from a solution of cadmium nitrate by oxalic acid. Cadmium bromide was prepared first by heating the metal in a combustion tube and passing bromine vapor over it, the bromide subliming to the cooler part of the tube. However, it was found later to be more convenient to dissolve the metal in bromine water. The bromine in

both cases was purified by distillation from potassium bromide.

The hydrochlorides of the methylamines (Bender and Hobein's preparations) were used as the sources of the bases.

Tetramethylammonium hydroxide was prepared from the iodide by Hofmann's original method.¹ A moderately dilute solution of the iodide was gently warmed, and shaken up with moist silver oxide until further additions of the dark brown oxide were no longer changed to the yellow silver iodide. The solution was then filtered and afterwards found to be free from iodine.

The bases were neutralized with the required acids, and the solutions were then concentrated to a convenient bulk.

Methods of Analysis.

The objections which Muspratt² raises to the established method of determining cadmium were not confirmed by my experience.

Preliminary experiments were made in which cadmium, known to be very pure, was used. A weighed quantity was dissolved in hydrochloric acid and the solution was diluted to a known volume.

Portions were drawn off and analyzed. In every case the analyses were perfectly satisfactory.

The method used in determining cadmium is as follows: Dilute solutions were heated to a temperature near boiling, and a strong solution of potassium carbonate was added, drop by drop, with constant stirring. After boiling a few minutes and allowing the beaker to stand, the whitish translucent precipitate of basic cadmium carbonate settled to the bottom, leaving the supernatant liquid perfectly clear.

A Gooch crucible was used in all cases for filtration. After washing several times by decantation, the precipitate was thrown on the filter and washed with several hundred cc. of boiling water. The Gooch crucible, without a cap, was then placed on a platinum plate in an iron crucible, dried at a

¹ Ann. Chem. (Liebig), **78**, 263.

² J. Soc. Chem. Ind., **13**, 211.

moderate heat, and then heated to dull redness for ten or fifteen minutes.

The halogens were determined by Mohr's and Volhardt's volumetric methods, and gravimetrically. When the silver halides were weighed a Gooch crucible was used, and the precipitate was dried in an air-bath at 140° .

Preparation of the Double Salts.

Concentrated solutions of the two salts were made, and from the calculated amounts present in each, such volumes of the two solutions were taken as to vary the molecular proportions in the different beakers, thus :

1 : 1 ; 1 : 2 ; 1 : 3 ; 1 : 4 ; 2 : 1 ; 3 : 1 ; 4 : 1.

Other proportions were used in cases which seemed to justify the use of larger differences in amounts. The mixtures were acidulated with the corresponding acid, and put in vacuum desiccators over sulphuric acid and caustic soda. The successive crops of crystals were analyzed as long as they appeared homogeneous. The microscope was constantly used to ascertain this.

Further particulars will be noted in the descriptions of the individual double salts.

Compounds Described.

- 2 : 1 Methylamine chlorcadmate.
- 1 : 1 Methylamine bromcadmate.
- 2 : 1 Methylamine bromcadmate.
- 1 : 1 Dimethylamine chlorcadmate.
- 1 : 2 Dimethylamine chlorcadmate.
- 3 : 2 Dimethylamine chlorcadmate.
- 1 : 1 Dimethylamine bromcadmate.
- 2 : 1 Dimethylamine bromcadmate.
- 1 : 4 Dimethylamine bromcadmate.
- 1 : 1 Dimethylamine iodocadmate.
- 1 : 1 Trimethylamine chlorcadmate.
- 3 : 2 Trimethylamine chlorcadmate.
- 1 : 1 Trimethylamine bromcadmate.

- 3 : 2 Trimethylamine bromcadmate.
 1 : 1 Trimethylamine iodocadmate.
 2 : 1 Trimethylamine iodocadmate.
 1 : 1 Tetramethylammonium chlorcadmate.
 1 : 1 Tetramethylammonium bromcadmate.
 2 : 1 Tetramethylammonium bromcadmate.
 1 : 1 Tetramethylammonium iodocadmate.
 2 : 1 Tetramethylammonium iodocadmate.

METHYLAMINE SALTS.

Double Chlorides.

2:1 Methylamine chlorcadmate.—When solutions of cadmium chloride and methylamine hydrochloride are mixed so that the number of molecules of the former to those of the latter bear these ratios: 2 : 1; 1 : 1; 1 : 2; 1 : 3; 1 : 4 the same double salt crystallizes out in every case.

Usually three or four successive crops of crystals from each beaker were obtained. The crystals are tabular, transparent, with a fibrous fracture, resembling selenite in general appearance. The cleavage is perfect, parallel to the broad faces, giving thin, pearly flexible, laminae.

Unsuccessful efforts were made to get specimens for crystallographic work. The general appearance of the crystals would indicate that they are isometric in form.

The solutions from which these crystals were obtained were very concentrated. The mother-liquor was drained off as thoroughly as possible, and the crystals quickly washed with water, pressed between layers of smooth drying paper, and dried in the air.

The analyses were quite concordant.

From beakers in which cadmium chloride was in a large excess, there were some indications of another double salt, when the solution was evaporated nearly to dryness. Under the microscope were noticed very small rod-shaped crystals in company with the silky needles of cadmium chloride. It was found impossible to get this salt in a pure form for analysis. When water was added to the syrupy mass of mixed crystals

and concentrated mother-liquors, the crystals were at once dissolved.

I. 0.1518 gram salt gave 0.2730 gram AgCl.

0.3151 gram salt gave 0.1262 gram CdO.

II. 0.0811 gram salt gave 0.1463 gram AgCl.

0.1498 gram salt gave 0.0601 gram CdO.

	Calculated for [NH ₃ (CH ₃) ₂] ₂ CdCl ₄ .	I.	Found. II.
Cl	44.55	44.42	44.55
Cd	35.24	35.04	35.10

Double Bromides.

1 : 1 Methylamine Bromcadmate.—This salt is so exceedingly soluble that it gave much trouble to get it sufficiently pure for analysis. From solutions in which cadmium bromide was in the ratios 1 : 1, 2 : 1, 3 : 1, etc., to the hydrobromide of the amine, long flattened prisms with rectangular terminations were obtained. The crystals were transparent, generally very much striated, and little could be determined as to their crystal form. The very concentrated mother-liquors from which they crystallized were always colored more or less with free bromine. In order to get the salt in a pure condition, it was found necessary to get it in sufficient quantities to permit of a hasty washing. By this very wasteful process enough was gotten for analysis in two instances. Other analyses were sufficiently close on cadmium to recognize this salt.

I. 0.3040 gram salt gave 23.65 × 0.00801 Br.

0.3040 gram salt gave 0.1038 gram CdO.

II. 0.2240 gram salt gave 0.3319 gram AgBr.

0.2766 gram salt gave 0.0957 gram CdO.

	Calculated for [NH ₃ (CH ₃) ₂] ₂ CdBr ₂ .	I.	Found. II.
Br	62.41	62.30	62.97
Cd	29.23	29.95	29.87

2 : 1 Methylamine Bromcadmate.—From solutions of methylamine hydrobromide and the metallic bromide mixed in the proportions 2 : 1, 3 : 1, 4 : 1, respectively, there sepa-

rated from the syrupy liquid, on concentration, large tabular crystalline masses, the edges of which were fringed with dendritic forms. No well defined individual crystals were obtained. Little trouble was experienced in getting this salt in a pure condition for analysis, and a number of concordant results were gotten.

I. 0.3593 gram salt gave 0.0932 gram CdO.

0.3552 gram salt gave 0.5394 gram AgBr.

II. 0.2860 gram salt gave 0.0746 gram CdO.

0.2249 gram salt gave 18.09 $\times$ 0.00801 Br.

	Calculated for [NH ₂ (CH ₃) ₂] ₂ CdBr ₄ .	I.	Found. II.
Cd	22.58	22.69	22.79
Br	64.51	64.54	64.42

Double Iodides.

Solutions of methylamine hydroiodide and cadmium iodide were mixed in the usual proportions and allowed to evaporate slowly.

In the beakers containing cadmium iodide in large excess, this salt crystallized out unchanged. In the other beakers, after the solutions had nearly reached dryness, a mixture of exceedingly soluble crystals was obtained. It was found impossible to effect a separation by mechanical means. The shiny hexagonal plates of cadmium iodide were easily recognized. Among these were some transparent crystalline aggregates of a different order of crystallization from the latter. Some of these were gotten out and dried as well as possible on filter paper. Qualitative experiments showed the presence of considerable quantities of cadmium.

DIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Dimethylamine Chlorcadmate.—This salt is readily obtained from very concentrated solutions of dimethylamine hydrochloride and cadmium chloride mixed in the molecular proportions 1 : 1, 2 : 1, and 1 : 2, respectively.

The crystals obtained under different conditions differ markedly in appearance. The forms most frequently met with were long, striated, flattened prisms, obliquely terminated. Some large flattened rhombohedral prisms crystallized

in a solution which was slowly evaporated for several months. Some of these were over two inches long.

Owing to the extremely concentrated solutions from which this salt comes down, the analyses in many instances were not very sharp.

However, recrystallized specimens gave results quite close to the theoretical. When heated to about 180° this salt sublimes slightly, at 240° it begins to darken, and at 261° – 262° it melts quite sharply with signs of decomposition.

- I. 0.5064 gram salt gave 0.2461 gram CdO.
0.2780 gram salt gave 0.4516 gram AgCl.
- II. 0.1521 gram salt gave 0.0733 gram CdO.
0.2075 gram salt gave 0.3368 gram AgCl.

	Calculated for $[\text{NH}_2(\text{CH}_3)_2]\text{CdCl}_2$.	I.	Found. II.
Cd	42.36	42.52	42.16
Cl	40.17	40.12	40.09

1 : 2 Dimethylamine Chlorcadmate.—This salt in general appearance is somewhat similar to the last described double halide, however, its flattened, lath-shaped, transparent crystals are not so obliquely terminated. It comes down from concentrated mixtures of solutions of the two constituents in which cadmium chloride is in excess. From a mixture in the ratio 1 : 2, one crop of crystals of the 1 : 1 salt was obtained. The successive crops were the 1 : 2 salt.

The salt was drained as thoroughly as possible from mother-liquors, quickly washed with water, and pressed between folds of smooth drying paper, as it was found to be slightly efflorescent, it was not air-dried, but weighed immediately.

The apparatus used for determining water of crystallization consisted of an air-bath through which was extended a piece of combustion tube. At either end were U-tubes containing glass beads moistened with sulphuric acid. Dried air was drawn over the salt which was placed in a porcelain boat in the tube.

A constant weight was obtained with the salt in question after heating one hour at 110° . No further loss was noted on raising the temperature to 125° . At 170° there were signs of

sublimation in the cold parts of the tube, but the loss in weight of the salt was very small. No signs of decomposition were apparent at 270° , when heated in a melting-point capillary tube.

I. 0.2466 gram gave 0.1412 gram CdO.

0.1092 gram gave 0.1739 gram AgCl.

0.6818 gram lost 0.0512 gram H_2O at 110° .

0.1291 gram gave 0.0738 gram CdO.

0.2093 gram gave 0.3341 gram AgCl.

1.3653 grams lost 0.1026 gram H_2O at 110° .

	Calculated for [$NH_2(CH_3)_2$]Cd ₂ Cl ₅ ·2H ₂ O.	Calculated for $NH_2(CH_3)_2Cd_2Cl_5$.	I.	Found. II.
Cd		50.06	50.10	50.01
Cl		39.56	39.33	39.42
H ₂ O	7.44		7.50	7.52

3 : 2 Dimethylamine Chlorcadmate.—From mixed solutions of the constituent halides made up in the proportions 2 : 1, 3 : 1, and 4 : 1, dimethylamine hydrochloride being in excess, no crystals appeared until evaporation had proceeded nearly to dryness.

The crystal forms usually met with under these circumstances were flat, transparent prisms having a rectangular cross section, the corners of which were symmetrically truncated. The solution at this stage of concentration was syrupy in its consistency. After draining off the mother-liquors as thoroughly as possible, the crystals were washed with water. This seemed to cause a slight superficial decomposition, the transparent crystals being rendered somewhat translucent.

Inasmuch as salts of analogous composition have not been met with hitherto, it was thought at first that the presence of impurities had affected the analyses. Comparing the results obtained with the formula given below, it was found that the figures for chlorine were always fair, but some of the cadmium percentages were markedly low. The lowest result obtained was 35.36 per cent. It is not at all probable that this can be the 2 : 1 salt—Cd 32.3 per cent—for it was noted that the analyses made under the best conditions gave higher results for the metal than in the other cases. From a solution made up in the proportion 4 : 1, the amine hydrochloride being in

excess, a crop of crystals which seemed to be homogeneous was obtained. These, on analysis, gave perfectly satisfactory results. The maximum and minimum results in the analysis of this double halide obtained from different sources are recorded below.

- I. 0.1430 gram salt gave 0.0578 gram CdO.
 0.0655 gram salt gave 0.1073 gram AgCl.
 II. 0.4003 gram salt gave 0.1667 gram CdO.
 0.1477 gram salt gave 0.2437 gram AgCl.

	Calculated for $[\text{NH}_2(\text{CH}_3)_2]_3\text{Cd}_2\text{Cl}_7$.	I.	Found. II.
Cd	36.70	35.36	36.43
Cl	40.62	40.45	40.75

Double Bromides.

1 : 1 Dimethylamine Bromcadmate.—When solutions of dimethylamine hydrobromide are mixed with equal, and with larger molecular quantities of cadmium bromide, and the resulting solutions are allowed to evaporate spontaneously, in some instances crystals in the form of fine white needles appeared. Under other conditions long, thin, striated prisms were obtained. The analyses would indicate that they were the same salt, though the needles were as much as two per cent. higher on cadmium. By diluting and allowing the solution to evaporate very slowly, it was usually possible to get out the larger crystals, which, owing to their compact form, could be better freed from mother-liquors and dried. If the first crop of crystals is allowed to remain in the solution 1 : 4, and the solution is still further concentrated, thick, short, transparent, octahedral grains, several mm. across, appear mixed with the flattened lath-shaped crystals of the 1 : 1 type. A discussion of these will be taken up later.

From the solutions made up in the ratios 1 : 1 and 1 : 2 only the 1 : 1 double bromide was obtained.

- I. 0.2603 gram salt gave 0.0857 gram CdO.
 0.1124 gram salt gave 0.1602 gram AgBr.
 II. 0.3768 gram salt gave 0.1225 gram CdO.

	Calculated for $\text{NH}_2(\text{CH}_3)_2\text{CdBr}_2$	I.	Found. II.
Cd	28.20	28.80	28.44
Br	60.21	60.56	...

2 : 1 Dimethylamine Bromcadmate.—In all cases where the hydrobromide of the amine was in excess, tabular crystalline masses with projecting rhombohedral prisms were obtained. The solutions were concentrated until they were of a syrupy consistency before any crystals appeared. Several crops from the different beakers were drained and dried and the whole recrystallized from water solution, acidulated with hydrobromic acid. The recrystallized specimens in all cases gave sharp results.

I. 0.2438 gram salt gave 0.0604 gram CdO.

0.1419 gram salt gave 0.2037 gram AgBr.

II. 0.3122 gram salt gave 0.0765 gram CdO.

0.1113 gram salt gave 0.1602 gram AgBr.

	Calculated for $[\text{NH}_2(\text{CH}_3)_2]_2\text{CdBr}_4$	I.	Found. II.
Cd	21.42	21.67	21.44
Br	60.96	61.00	61.17

1 : 4 Dimethylamine Bromcadmate.—When solutions in which the hydrobromide of the base bears the ratios 1 : 4, 1 : 5, etc., to the cadmium bromide are allowed to evaporate spontaneously, there first appears a crop of long striated, prismatic crystals, which prove on analysis to be the 1 : 1 double bromide. If, without removing these, the solution is still further concentrated, under the crystalline crust formed as the solution approaches dryness, short, thick, brilliant crystals appear. These are hard and compact, and may be washed by picking them out one by one on a platinum spatula and dipping them momentarily in a beaker of water. When water is added to the mixture of crystals mentioned above, all quickly dissolve except the short, thick grains. The latter become somewhat opaque, owing to a slight surface decomposition. The analyses were not all concordant, but were fair considering the conditions under which the salt was obtained. The lowest result for cadmium recorded below was from an analysis of a recrystallized specimen of the salt.

- I. 0.2458 gram salt gave 0.1051 gram CdO.
 0.1640 gram salt gave 0.2279 gram AgBr.
 II. 0.2296 gram salt gave 0.0955 gram CdO.

	Calculated for [NH ₂ (CH ₃) ₂]Cd ₄ Br ₉ .	I.	Found. II.
Cd	36.98	37.41	36.39
Br	59.21	59.05	

Double Iodides.

1 : 1 Dimethylamine Iodocadmiate.—From solutions containing dimethylamine hydroiodide and cadmium iodide in the ratios 1 : 1 and 1 : 2, respectively, tabular, cubical, crystalline masses appeared when the solution had become quite concentrated. The crystals were lifted out, dipped in water, and quickly dried between folds of filter paper.

When cadmium iodide was in large excess it crystallized out unchanged from the mixed solutions. In the beakers containing the hydroiodide of the amine in excess, crystals appeared only after the solutions had reached a somewhat viscous state. It was found impossible to get them out in a condition approximating purity, so no analyses were made. Alcohol was then tried as a solvent, but with no better results.

0.2938 gram salt gave 0.0703 gram CdO and 0.3828 gram AgI.

	Calculated for [NH ₂ (CH ₃) ₂]CdI ₃ .	Found.
Cd	20.84	20.93
I	70.60	70.35

TRIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Trimethylamine Chlorcadmate.—This salt has already been described and its crystallographic properties investigated by Hjørtdahl.¹ It crystallizes from all the mixtures tried, 4 : 1 to 1 : 4, inclusive. When the solutions of the two constituents are rather concentrated, on mixing, the double halide comes down as a white crystalline precipitate.

¹ Zeit. für Kryst., 6, 466; Jahr., 1882, 475.

This is sparingly soluble in cold water, easily soluble in warm. From the solution, on standing, beautiful, transparent, monoclinic prisms, several mm. across, appear. These often assume a pseudo-hexagonal form. Twinning is also quite frequent. The salt crystallizes unchanged from water solution. There were no signs of decomposition when the salt was heated to 270° .

0.4146 gram salt gave 0.1903 gram CdO.

0.3861 gram salt gave 0.5951 gram AgCl.

0.4285 gram salt gave 0.1968 gram CdO.

0.4818 gram salt gave 0.8711 gram AgCl.

	Calculated for [NH(CH ₃) ₃] ₂ CdCl ₃ .	I.	Found. II.
Cd	40.23	40.16	40.18
Cl	38.15	38.07	38.01

3 : 2 Trimethylamine Chlorcadmate.—After one crop of crystals of the 1 : 1 double chloride above described had been obtained from the solution made up in the ratio 4 : 1 (amine in excess), there appeared, on further concentration, obliquely terminated, flattened prisms. Inasmuch as the formula to which the analyses agreed is an unusual one, it was thought that possibly it might be the 2 : 1 salt, and that the discrepancy in cadmium might arise from impurities. The work was repeated several times, and there seems to be little doubt that the formula below correctly represents the compound. Enough was obtained to admit of a hasty washing with water.

The analyses made under the most favorable conditions give a higher percentage for cadmium than in the other cases. This would indicate that the impurities tend to lower the percentage of cadmium in the compound, which argues against its being the 2 : 1 salt.

0.1111 gram salt gave 0.0429 gram CdO.

0.1338 gram salt gave 0.2053 gram AgCl.

0.0693 gram salt gave 0.0268 gram CdO.

0.0693 gram salt gave 0.1066 gram AgCl.

	Calculated for [NH(CH ₃) ₃] ₃ Cd ₂ Cl ₇ .	I.	Found. II.
Cd	34.34	33.78	33.88
Cl	37.99	37.90	37.99

Double Bromides.

1 : 1 Trimethylamine Bromcadmiate.—Hiortdahl¹ has described the crystallographic properties of this salt in an article previously referred to. When a mixture of solutions of trimethylamine hydrobromide and cadmium bromide in which the latter is in excess, is concentrated to such an extent that crystals are formed on cooling, a network of long, thin, prismatic crystals separate. These are apparently homogeneous, but no concordant results can be obtained when the crystals are in this form. It is probable that the high percentage for cadmium found is to be explained by the fact that the crystals in this form presented a large surface, which prevented the perfect separation of the mother-liquors, rich in cadmium bromide. From these same solutions on slow evaporation, short, thick, skeleton crystals, apparently pseudo-hexagonal in form were obtained. The analyses of these were satisfactory in all cases.

I. 0.2627 gram salt gave 0.0819 gram CdO.

0.2071 gram salt gave 0.2825 gram AgBr.

II. 0.1550 gram salt gave 0.0482 gram CdO.

	Calculated for [NH(CH ₃) ₃]CdBr ₃ .	I.	Found.	II.
Cd	27.24	27.27		27.14
Br	58.16	57.97		

3 : 2 Trimethylamine Bromcadmiate.—When the hydrobromide of the amine was in excess in mixed solutions of cadmium bromide and the former, the above double bromide was obtained. The first crops of crystals on analysis gave high results for cadmium, but the successive crops agreed closely with the assigned formula.

The form of the crystals varied widely with the conditions under which they were obtained. Those giving the most concordant results were narrow, flattened, transparent prisms, terminating in pyramidal planes.

The first crops of long, white, striated prisms which gave high analyses for cadmium, on recrystallization gave fair results. In all cases when recrystallization was resorted to, the percentage of cadmium was *lowered*.

¹ Zeit. für Kryst., 6, 467; Jahr., 1882, 475.

- I. 0.2680 gram salt gave 0.0716 gram CdO.
 II. 0.2384 gram salt gave 0.0639 gram CdO.
 0.1243 gram salt gave 0.1702 gram AgBr.
 0.5039 gram salt gave 11.56×8.104 mgms. $\text{N}(\text{CH}_3)_3$.

	Calculated for $[\text{NH}(\text{CH}_3)_3]_3\text{Cd}_2\text{Br}_7$.	I.	Found. II.
Cd	23.28	23.32	23.45
Br	58.00	58.17	
$\text{N}(\text{CH}_3)_3$	18.40	18.58	

Double Iodides.

1 : 1 Trimethylamine Iodocadmiate.—This salt crystallizes in splendid large cubical masses, resembling potassium iodide in general appearance. From some of the beakers only individual transparent cubes were gotten. These presented a remarkable play of colors in the sunlight. The solutions from which this salt crystallized were made up in the ratios 1 : 1, 1 : 2, 1 : 3, etc.; *i. e.*, cadmium iodide in equal and in larger molecular quantities.

- I. 0.2055 gram salt gave 0.0480 gram CdO.
 II. 0.4505 gram salt gave 0.1028 gram CdO.
 0.1141 gram salt gave 0.1458 gram AgI.

	Calculated for $[\text{NH}(\text{CH}_3)_3]\text{CdI}_3$.	I.	Found. II.
Cd	20.30	20.43	19.97
I	68.81		69.00

2 : 1 Trimethylamine Iodocadmiate.—When the molecular ratios of the two halides, trimethylamine hydroiodide and cadmium iodide, stand to each other 2 : 1, 3 : 1, etc., in solution, and the mixture is allowed to evaporate slowly, very beautiful transparent crystals appear. These are usually modified rhombic prisms. The crystals separated out as individuals in every case. In some instances the 1 : 1 and 2 : 1 double iodides crystallized out side by side in the same beaker. But the difference in crystal form admitted of an easy separation by mechanical means.

Both of the latter salts are much less soluble in water than the above described trimethylamine double bromides.

- I. 0.3689 gram gave 0.0643 gram CdO.
 II. 0.3022 gram gave 0.0524 gram CdO.
 0.1140 gram gave 0.1451 gram AgI.

	Calculated for [NH(CH ₃) ₃] ₂ CdI ₄ .	I.	Found.	II.
Cd	15.17	15.25		15.13
I	68.56	68.72		

TETRAMETHYLAMMONIUM SALTS.

Double Chlorides.

1 : 1 Tetramethylammonium Chlorcadmate.—This double salt crystallized in magnificent hexagonal prisms several cm. long. It was obtained from every mixture of the constituent halides experimented with. When the mixed solutions were concentrated to such an extent that crystals were formed on cooling, the results obtained on analysis were not sharp. The slender white columnar crystals formed under such circumstances seemed to hold the mother-liquors with great persistence. On recrystallization the percentage for cadmium accorded with the assigned formula below. The double salt in the form of the hexagonal prisms above mentioned always gave sharp results. This compound crystallizes from water unchanged.

Inasmuch as there are double bromides and double iodides formed in the ratio 2 : 1, it was thought that an analogue might be gotten in this series; but there were no evidences of a salt of this composition. From a solution containing mixtures of the two chlorides in the proportion 4 : 1, the ammonium salt in excess, four successive crops of the 1 : 1 compound were gotten before evaporation had proceeded to such an extent that nothing definite could be further isolated from the mother-liquor.

- 0.4074 gram gave 0.1780 gram CdO.
 0.1613 gram gave 0.2361 gram AgCl.
 0.2054 gram gave 0.0893 gram CdO.

	Calculated for [N(CH ₃) ₄] ₂ CdCl ₂ .	I.	Found.	II.
Cd	38.29	38.23		38.04
Cl	36.32	36.15		

*Crystallography.*¹

Hexagonal.

$$P : P = 142^{\circ} 15'$$

$$P : \infty P = 130^{\circ} 21'$$

$$\infty P : \infty P = 120^{\circ}$$

$$\text{Axis } c' = 0.734872$$

Double Bromides.

1 : 1 Tetramethylammonium Bromcadmate.—When concentrated water solutions of cadmium bromide and tetramethylammonium bromide are mixed in the cold in any of the ratios 4 : 1–1 : 4, inclusive, a white crystalline precipitate is formed. The precipitates thus formed were redissolved and the solutions diluted. On slow evaporation large, transparent, hexagonal prisms terminating in pyramidal faces were obtained. These very much resemble the double chloride last described. This salt is readily obtained quite pure. The analyses in all instances were consistent with each other and corresponded to the calculated value below.

0.3637 gram gave 0.1094 gram CdO.

0.2452 gram gave 0.3240 gram AgBr.

0.1822 gram gave 0.0547 gram CdO.

	Calculated for [N(CH ₃) ₄]CdBr ₃ .	I.	Found. II.
Cd	26.34	26.31	26.26
Br	56.24	56.15	

2 : 1 Tetramethylammonium Bromcadmate.—From mixed solutions of the two bromides in which tetramethylammo-

¹ I am indebted to Dr. F. P. King, of the Department of Mineralogy, for the crystallographic work. I would take this occasion to express my thanks.

nium bromide was in excess several crops of the 1 : 1 double bromide were first obtained, but finally short, imperfect, flattened rhombic prisms appeared after the solutions had been further concentrated. Mechanical separation had to be used in some cases.

When the crystals were homogeneous the analyses were always close for the formula assigned.

0.2777 gram gave 0.0612 gram CdO.

0.1822 gram gave 0.2359 gram AgBr.

0.1575 gram gave 0.0349 gram CdO.

	Calculated for [N(CH ₃) ₄] ₂ CdBr ₄ .	I.	Found.	II.
Cd	19.35	19.28		19.38
Br	55.08	55.02		

Double Iodides.

1 : 1 Tetramethylammonium Iodocadmiate.—Like the analogous double bromide of tetramethylammonium, this salt is sparingly soluble in cold water. From dilute solutions of the two iodides, in which cadmium iodide is in excess, a white coating of individual crystalline grains appear on the sides and the bottom of the beakers containing the mixture. The crystal form of the grains, some of which were of microscopic size, was rather indefinite. From the mother-liquor poured off the crystals, there appeared another crop of the same in a very short time, on standing.

In some of the succeeding crops of crystals, the characteristic double iodide 2 : 1 described below was noticed.

No evidence of a double salt having a higher proportion of cadmium iodide was obtained. From a solution containing 625 mgms. of tetramethylammonium iodide and 15 grams of cadmium iodide only the 1 : 1 double iodide came down on slow evaporation.

I. 0.2981 gram gave 0.0665 gram CdO.

0.1786 gram gave 0.2213 gram AgI.

II. 0.2467 gram gave 0.0559 gram CdO.

	Calculated for [N(CH ₃) ₄]CdI.	I.	Found.	II.
Cd	19.80	19.51		19.82
I	67.10	66.91		

2 : 1 *Tetramethylammonium Iodocadmiate*.—The crystals of this salt usually appeared as white, feathery, individual crystals terminating in a very acute angle. These covered the walls and the bottom of the beaker as a crystalline coating. When the first crop had been gotten out and the mother-liquor had been allowed to evaporate spontaneously, tabular, transparent crystals, several mm. broad, were formed. These were imperfect, but their general outline seemed to indicate that they were modified tetrahedra. Both this salt and the one last described are very brilliant, and exhibit a remarkable play of colors in the sunlight. The beakers from which the compound was obtained contained an excess of tetramethylammonium iodide. In some cases the two double halides, 1 : 1 and 2 : 1, were noticed in the same beaker. The crystals were too small to be separated conveniently by mechanical means, but the crystal forms were easily recognizable.

I. 0.4543 gram gave 0.0762 gram CdO.

0.3559 gram gave 0.4348 gram AgI.

II. 0.2866 gram gave 0.0476 gram CdO.

	Calculated for [N(CH ₃) ₄] ₂ CdI ₄ .	I.	Found. II.
Cd	14.62	14.67	14.53
I	66.05	65.94	

Conclusions.

(1). It has been seen that all the double halides of the alkali metals and ammonium with cadmium, described in the literature, may be classified under the types: 1 : 1, 2 : 1, 3 : 1, 4 : 1.

Among the double halides described in this paper, the types met with are 1 : 2, 2 : 1, 3 : 2, 1 : 2, 1 : 4.

Of these it will be noted that the last three types have no analogues among the double halides of the alkali metals and ammonium with cadmium.

(2). No double halides corresponding to (NH₄)₄CdCl₆ and (NH₄)₄CdBr₆, *i. e.*, the 4 : 1 type were obtained.

(3). Of the 21 compounds described in this paper, 18 conform to the law of Remsen. Three fall under the extension of the law.

BIOGRAPHICAL.

The author of this dissertation was born at Harmony, Va., Feb. 5, 1869. His early education was received at public and private schools in Halifax County, Va. In 1885 he entered Randolph Macon College, and in 1890 he received the degree of A. M. from that institution. For the four succeeding years he taught in the preparatory department of this college at Bedford City, Va. Since October, 1894, he has been pursuing advanced work in chemistry at the Johns Hopkins University, having taken mineralogy and physics as his subsidiary studies.

During the year 1896-7 he has been a fellow in the department of chemistry. In June, 1895, he was elected Professor of Chemistry in Randolph Macon College, and granted two years' leave of absence to complete his course of studies already begun.

